Predicting the Bizarre Properties of Plutonium

PLUTONIUM is arguably the most complex element known, and it is one of the least well understood. Before it liquefies, plutonium exhibits six solid material phases that vary considerably in density. Plus, a seventh phase may appear when the radioactive metal is under pressure.

To understand material phases, think of carbon and its most common solid phases: soft graphite and hard diamond. Both are made of carbon atoms, but the bonds that form between the atoms create two very different materials. Many elements have two or more solid phases, but most have no more than four. With six phases, solid plutonium is highly unusual.

The material's peculiarities do not stop there. Experiments over the years have demonstrated other anomalous properties, including an almost complete absence of magnetism and highly unusual resistivity.

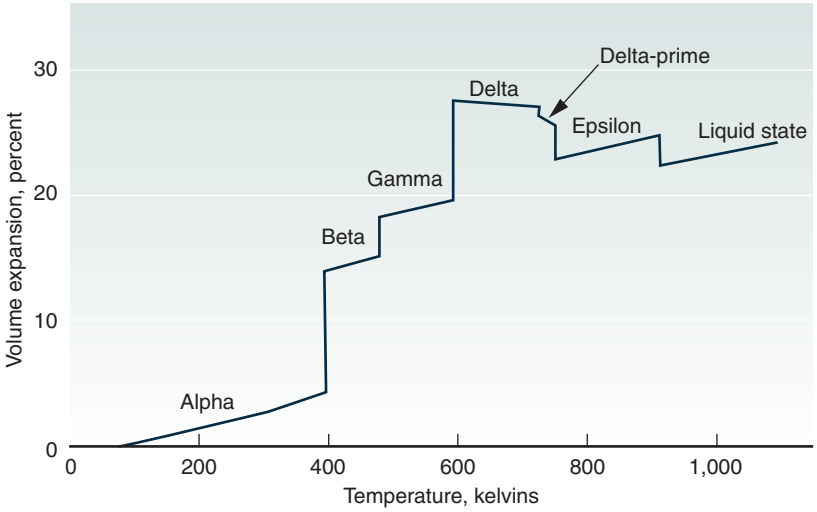
Solid plutonium is most malleable in the delta phase. People who work with plutonium—fabricating pits for nuclear weapons, for instance—use it in this phase. However, the delta phase of pure plutonium is stable only between 500 and 700 kelvins, well above the 300 kelvins of room temperature. Decades ago, weapons researchers discovered that plutonium would remain in a stable delta phase at room temperature when it is mixed with a small amount of gallium or certain other elements.

The Power of Atlas

In an effort to explain some of plutonium's strange behavior and better understand results from past experiments, a team of Lawrence Livermore scientists and international collaborators used the Laboratory's Atlas supercomputer to perform some of the most precise predictions yet of delta-phase plutonium. For these simulations, the team combined density functional theory (DFT) and dynamical mean field theory (DMFT) to calculate plutonium's delta-phase electronic structure, specifically its lack of magnetic "susceptibility."

All atoms have one or more electrons spinning around a nucleus in orbits called shells. Plutonium is one of several materials with electrons in a very narrow shell called 5*f*. The shell is so narrow and the influence of each electron on the others in the shell is so strong that no single electron can be treated independently. As a result, electron behavior in the 5*f* shell is "strongly correlated." Other strongly correlated substances include iron, nickel, many oxides, and high-temperature superconducting materials. Small changes in their control parameters often result in disproportionately large responses.

While DFT is useful for explaining the energy and interactions of many electronic systems, it may break down for certain properties of strongly correlated systems. Previous research combining the

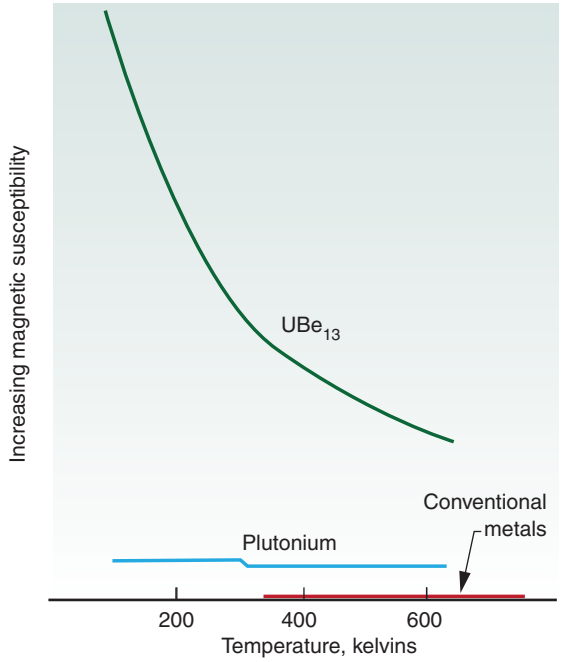


As temperature increases, plutonium's volume changes dramatically before it becomes a liquid. The radioactive metal is unique among elements in exhibiting six solid phases at ambient pressure.

two theories to simulate delta-phase plutonium could obtain only approximate solutions to the DMFT equations. Recent advances in the continuous-time quantum Monte Carlo method—and the Atlas computer—allowed exact solutions for the first time.

"This work would have been impossible without Atlas," says physicist Chris Marianetti, who led the computational effort. Atlas can process 44-trillion floating-point operations per second and is one of the Laboratory's workhorses for high-end, unclassified computing. This project was one of 17 Computing Grand Challenge initiatives selected in 2007 and was funded by Livermore's Laboratory Directed Research and Development (LDRD) Program.

"We used DMFT to treat plutonium's 5*f* electrons and DFT for electrons in the other shells," says Marianetti. He worked with the same combination of theories in his Ph.D. research at the Massachusetts Institute of Technology, where he studied the electronic correlations in cobalt oxide, one of the materials inside rechargeable batteries for cell phones, MP3 players, and other electronic devices.



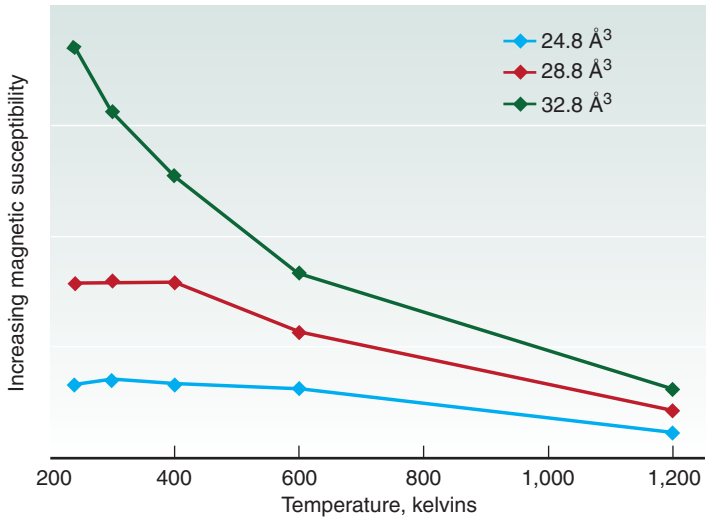
The magnetic susceptibility of plutonium is unusual. For conventional metals such as molybdenum, titanium, and platinum, magnetism does not change with temperature (red curve). Strongly correlated materials, however, are more magnetic at low temperatures than they are at higher temperatures. The green curve shown for uranium–beryllium-13 (UBe_{13}) is typical. Plutonium's magnetic susceptibility (blue curve) lies between these cases.

Unusual Magnetic Attraction

In DMFT simulations, one atom is ripped from a lattice of atoms and put in a "bath" of fictitious electrons whose properties duplicate the average properties of the lattice. With a large lattice reduced to an averaged, single-site problem, DMFT can calculate the electronic structure for the entire strongly correlated lattice.

The grand-challenge team's simulations predicted that at room temperature with delta-phase plutonium at its equilibrium volume, the *f* electrons are delocalized. That is, they easily move about the lattice and are not associated with one particular atom. Under these conditions, the material's magnetic susceptibility is very low above 600 kelvins and only slightly higher at lower temperatures.

A change in temperature does not affect the magnetism of conventional metals such as platinum or molybdenum. In contrast, most strongly correlated materials other than plutonium exhibit a distinct relationship between temperature and magnetic susceptibility. Their magnetic susceptibility is high at low temperatures and lower at high temperatures. Experiments demonstrate, however, that plutonium's magnetic susceptibility is unlike that of other strongly correlated materials. In fact, it behaves more like a conventional metal, although it exhibits slight temperature dependence.



In the Livermore simulations, the volume of plutonium was increased, pulling the plutonium atoms farther apart. Only under these circumstances and at the largest volume does plutonium's magnetic susceptibility begin to mimic the temperature dependence of other strongly correlated materials such as UBe_{13}. (Å^3 = cubic angstroms, where 1 Å^3 equals 1×10^{-30} cubic meters.)

If the plutonium volume is expanded—if the lattice is stretched so that the *f* electrons are farther apart—the magnetic susceptibility of plutonium changes. The Livermore simulations showed that as the lattice expands, the *f* electrons become heavier, or localized. That is, they are more associated with one particular atom and thus cannot easily hop through the lattice. The plutonium is then a more strongly correlated material. The transition from delocalized to localized behavior occurs at increasingly lower temperatures as the lattice volume continues to expand. With greater distance between the electrons, delta-phase plutonium begins to behave more like other strongly correlated materials. As temperature drops, the metal's magnetic susceptibility increases.

Future Phases

The team intends to tackle plutonium's alpha phase next. Marianetti will continue to lead this simulation effort, but he will do so from afar. He was a postdoctoral researcher at the Laboratory until August 2008, when he joined the faculty of Columbia University. Livermore physicist Mike Fluss, who leads a larger LDRD project that includes the plutonium DMFT simulations, notes that Marianetti's expertise with DMFT is unique. "I look forward to a strong collaboration with Chris well into the future," says Fluss.

Predicting the behavior of alpha-phase plutonium will be more challenging than the delta-phase simulations. The smallest individual crystal in delta-phase plutonium contains one atom. In the alpha phase, 16 atoms make up the smallest crystal. Another challenge will be to explain the role that other materials play in stabilizing delta-phase plutonium. Only with the aid of powerful supercomputers can researchers answer plutonium's many riddles.

—Katie Walter

Key Words: Atlas supercomputer, Computing Grand Challenge Program, delta phase, density functional theory (DFT), dynamical mean field theory (DMFT), plutonium.

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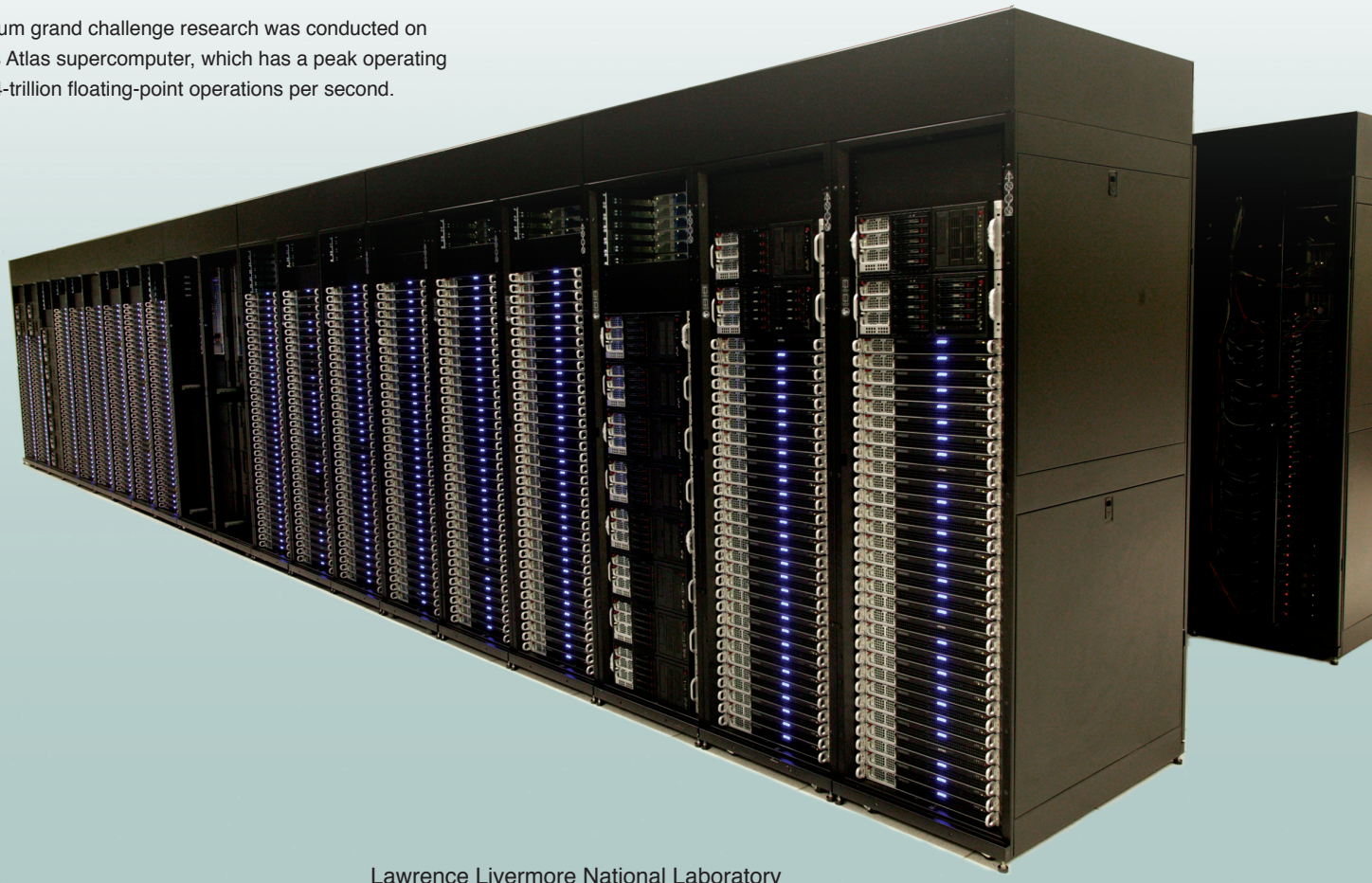
The plutonium grand challenge research was conducted on Livermore's Atlas supercomputer, which has a peak operating speed of 44-trillion floating-point operations per second.



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